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TRANSFORMATION REACTIONS AND MECHANICAL PROPERTIES OF ZIRCONIUM ALLOYS CONTAINING COPPER AND MOLYBDENUM

by

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SUMMARY OF RESULTS

Zirconium alloys containing from 1 to 2 wt% copper with from 1.5 to 2 wt% molybdenum and based on reactor-grade zirconium sponge were prepared by non-consumable (tungsten) inert-arc melting. These alloys respond to heat treatment, and ageing occurs through the mechanism:

$$\alpha' \rightarrow \alpha + \beta \rightarrow \alpha + \beta + \text{intermetallic}$$

All alloys in the composition range investigated were found to be readily hot workable at 800°C (1470°F) and on subsequent solution heat treatment at 750°C (1380°F), yield strengths of up to 123,000 psi were obtained.

INTRODUCTION:

Zirconium Alloys Containing Copper and Molybdenum

The low thermal neutron-capture cross section of zirconium, coupled with reasonably good mechanical properties and corrosion resistance have made this metal of great practical interest in nuclear engineering. The development of the zircaloy-type of alloy based on reactor-grade (low hafnium) zirconium with additions of tin, iron, chromium and nickel has resulted in widespread application with resultant accumulation of experience in production, fabrication and service performance, as well as the development of data on mechanical properties and corrosion behaviour under many conditions. At the present time zircaloy is generally considered to be the most attractive material available for water-cooled power reactor fuel cladding and core components such as pressure tubes, but projected power reactor designs already require a better material having improved mechanical properties and corrosion resistance at the higher operating temperatures contemplated.

It would be ideal if a new alloy could be developed which would combine good high temperature strength with good corrosion resistance, but an alternative would be acceptable, consisting of cladding a high strength core with a more corrosion resistant but weaker skin if no one alloy can be found which satisfies both conditions.

As part of the Canadian programme directed towards natural uranium fuelled power reactor development, a study of zirconium-base alloys containing between 1 and 2 wt% copper, combined with from 1.5 to 2.5 wt% molybdenum, has been made in these laboratories.

In this investigation, the effects of solution and ageing heat treatments have been examined with respect to metallographic structure and resulting room temperature mechanical properties. An assessment of hot working fabrication characteristics has also been made.

PROCEDURE

Preparation of Alloys

The alloys prepared for this investigation were made from reactor-grade zirconium sponge (Carborundum Metals Company, Albany, N.Y., Lot No RP 26). The copper used was OFHC copper with a purity of 99.99% and the molybdenum (Sylvania Electric Products Inc., Towanda, Pennsylvania) had a purity of 99.5%.

The alloys listed in Table 1 were prepared as 75 gram buttons melted in a small arc-melting furnace in an argon atmosphere using a tungsten electrode and a cold copper hearth. The loose zirconium sponge particles were first melted, in a circular mould, to convert from sponge to a solid metal button and then the copper and molybdenum were added in one remelting operation, followed by at least two remelts to insure homogeneity. The last two meltings were in a "cigar" shaped cavity, 2-1/4 inches in diameter.

Test Methods

The "cigar" shaped buttons were hot swaged in air at 800°C (1470°F) into 0.35 inch diameter rods.

Samples from the hot swaged rod for solution treatment were heated for one hour in Houghton 980 salt at temperatures from 600°C (1110°F) to 900°C (1650°F) and then quenched in water. Ageing of the solution-treated samples at 400°C (750°F) and 500°C (930°F) was done in air.

X-ray diffraction patterns of the solution-treated and aged samples were obtained on flat sections of the samples prepared by polishing on silicon carbide abrasive papers from 240 to 600 grit to remove about 1/8 inch of metal. To remove any worked metal due to the polishing, the samples were chemically polished in a solution containing:

45 cc glycerine

45 cc nitric acid

10 cc hydrofluoric acid

Samples for hardness testing were similarly prepared.

A dilatometric specimen, 2½ inches long by 5/16 inches in diameter, of the alloy Zr - 1.5 wt% Cu - 2.0 wt% Mo was machined from a hot swaged rod after annealing at 600°C (1110°F) for 24 hours at a vacuum of 0.01 microns.

Tensile specimens for the Hounsfield Tensometer (½ inch gauge length, 1/8 inch diameter) were machined from sections of the 0.35 inch diameter rods after they had received the required heat treatments.

Metallography

The metallographic technique consisted of rough polishing the samples on silicon carbide abrasive papers from 240 to 600 grit, then electro-polishing in a solution containing:

50 cc perchloric acid

175 cc acetic acid

100 cc ethylene glycol

This solution should be used in a water-cooled glass beaker and best results were obtained when the samples were constantly agitated.

A current density of 1 amp/cm^2 was applied for 30 seconds, and a stainless steel cathode was used. After polishing, the samples were rinsed in a 10% aqueous solution of acetic acid.

The electro-polish revealed the grain structure sufficiently so that no subsequent etching was necessary.

In the work reported here, the course of the ageing reactions of zirconium alloys containing copper and molybdenum in the composition range 1.0 to 2.0 wt% Cu, combined with 1.5 to 2.5 wt% Mo, was followed by hardness measurements which were considered in conjunction with metallographic examination and x-ray analysis to interpret their ageing transformation mechanism.

RESULTS

Solution Treatment

The results of a hardness survey of the alloys solution-treated at temperatures from 600°C (1110°F) to 850°C (1560°F) are given in Table 2 and are plotted graphically in Figure 1. Hardening in all the alloys commenced between 700°C (1290°F) and 750°C (1380°F), indicating that a phase transformation occurred in this temperature range and that a high temperature phase had been retained at room temperature. A thermal dilation curve for the alloy Zr - 1.5 wt% Cu - 2.0 wt% Mo (Figure 2) also shows a transformation at a temperature about 700°C (1290°F).

X-ray analysis of the alloy Zr - 1.5 wt% Cu - 2.0 wt% Mo, after solution treatment at 850°C (1560°F) and also after solution treatment at 800°C (1470°F) showed the presence of martensitically formed α'. Metallographic examination revealed a structure of α in a matrix of α' (Figures 3 and 4).

Figures 3 and 4 are typical microstructures of all the alloys

solution-treated at these temperatures. Samples solution-treated at 900°C (1650°F) showed a similar structure to those treated at 850°C (1560°F) except that there was less α present at the higher temperature. As the solution temperature was increased from 800°C (1470°F) to 900°C (1650°F) more α' and less α occurred.

Ageing Reaction

In order to follow the course of the ageing reaction of these alloys by means of hardness measurements, some of the alloys were solution-treated at 800°C (1470°F), 850°C (1560°F), 900°C (1650°F), and then aged at 400°C (750°F) and 500°C (930°F). Figures 5 to 10 inclusive, are the ageing curves (hardness versus time at temperature) of the alloys examined.

During the early stages of ageing at 400°C (750°F) a lack of ageing response was evident and little loss in hardness occurred after 200 hours of testing. When the ageing temperature was increased to 500°C (930°F) over-ageing began immediately, especially for the samples solution-treated at 850°C (1560°F) and 900°C (1650°F).

X-ray analysis of the alloy Zr - 1.5 wt% Cu - 2.0 wt% Mo solution-treated at 850°C (1560°F) and aged at 400°C (750°F) for 200 hours indicated the presence of α', α and β. This structure is shown in Figure 11. X-ray analysis of the same alloy solution-treated at 850°C (1560°F) and aged at 500°C (930°F) for 24 hours showed the presence of α, β and Zr_2Cu. Figure 12 is a photomicrograph of this structure.

Mechanical Properties

During the fabrication of test specimens, the alloys demonstrated good working properties at 800°C (1470°F) and the workability at this

temperature was exemplified by rolling the alloy Zr - 1.5 wt% Cu - 2.0 wt% Mo from a ½ inch thick button to a sheet 0.062 inch thick (87.6% reduction) with no edge cracking or other damage.

Room temperature tensile tests of the alloys were investigated after solution-treatment at 750°C (1380°F) and at 850°C (1560°F), as well as after solution-treating at 850°C (1560°F), followed by ageing for 200 hours at 400°C (750°F). The tensile specimens solution-treated at 850°C (1560°F) and also those solution-treated at this temperature and aged at 400°C (750°F) broke outside the gauge length at the change in section and at the shoulder of the test specimen. The properties of the specimens solution-treated at 750°C (1380°F) are given in Figure 13 and in Table 1. These specimens had good elongations with yield strengths up to 123,000 psi.

DISCUSSION

H.A. Robinson et al [1] [2] have shown zirconium alloys, in general, age similarly to titanium alloys. Zirconium alloys containing sufficient additions of β stabilizing elements, such as molybdenum, age by the following transformation:

$\beta \rightarrow \omega + \beta_r \rightarrow \beta_u + \alpha \rightarrow \alpha$ + intermetallic compound

ω - brittle transformation phase

β_r - partially enriched β

β_u - fully enriched β

α - equilibrium α

Alloys having insufficient β stabilizing alloying elements age by the following transformation:

$\alpha' \rightarrow \alpha + \beta_u$ or terminal solid solution

α' - formed martensitically from β

W. Chubb[3] showed the alloy Zr-4 wt% Sn - 1.6 wt% Mo could be heat treated to produce either the β phase or the martensitically formed acicular α', depending on the rate of cooling. Rapid quenching retained the enriched β phase, whereas air cooling produced an acicular α' zirconium. In the present work, x-ray analysis and metallographic examination indicated that the alloys solution-treated at 800°C (1470°F), 850°C (1560°F), and 900°C (1650°F) were quenched from the $\alpha+\beta$ phase region. Hardening occurred during the quenching so no evidence was available to explain the hardening mechanism. It is improbable that hardening occurred during the $\beta \rightarrow \alpha'$ transformation since the strains and volume changes occurring during this transformation would be insufficiently great to have an effect. Hardening may have been caused by the transformation of some α' to α and β during quenching and these phases could have been present in the quenched samples in either too small amounts to be determined by the x-ray diffraction or, in the case of α, the lines would be overshadowed by the broad diffused lines of the α' phase.

During the over-ageing of the samples after solution treatment, as the copper and molybdenum are known to be β soluble, the α' which was martensitically formed from the β would contain both copper and molybdenum in solid solution. On ageing, the α' transformed into $\alpha+\beta$ and the tendency would be for the β thus formed to contain the copper and molybdenum. Further ageing precipitated $ZrCu_2$ but the β would still be partially enriched with molybdenum still in solid solution.

In this report the x-ray analyses and metallographic structure of the Zr-1.5 wt% Cu - 2.0 wt% Mo alloy has been cited because this alloy was typical of the alloys in the composition ranges examined. There

was no noticeable difference in the structure of these alloys and they all reacted similarly to heat treatment, as is evident from the ageing curves.

Mechanical Properties

Examination of the ageing curves revealed that several combinations of heat treatments are possible which should produce mechanical properties between the brittle condition of the samples solution-treated at 850°C (1560°F) and the ductile condition of the samples solution-treated at 750°C (1380°F).

CONCLUSIONS

The zirconium-base alloys containing 1.0 to 2.0 wt% Cu, combined with 1.5 to 2.5 wt% Mo, are susceptible to heat treatment, and age according to the transformation:

$$\alpha' \rightarrow \alpha + \beta \rightarrow \alpha + \beta + \text{intermetallic}$$

These alloys have excellent hot swaging and rolling properties at 800°C (1470°F) and a wide range of room temperature mechanical properties appear to be available by varying the heat treatment. Solution heat treatment at 750°C (1380°F) produced yield strengths up to 123,000 psi, and the alloy Zr - 1.5 wt% Cu - 1.5 wt% Mo had a yield strength of 101,500 psi, with an elongation of 23%.

These alloys are more sensitive to heat treatment than to variations in composition.

Further investigations are being conducted to study the effect of various heat treatments on the structure and to correlate the structure with mechanical properties and with the corrosion resistance.

ACKNOWLEDGEMENT

This work was performed under the general direction of Mr. N. S. Spence, Head of the Nuclear Metallurgy Section. The production of alloy melts, heat treatment, and the preparation of metallographic specimens were performed by W. Hutchings. X-ray diffraction examinations were done by Mrs. S. J. Basinski, Metal Physics Section, whose assistance in interpreting the data, is acknowledged.

REFERENCES

1. H. A. Robinson, J. R. Doig, M. W. Mote and P.O. Frost. Heat Treatment, Transformation Reactions, and Mechanical Properties of Some High-Strength Zirconium-Base Alloys, Trans. AIME 215, 237 (April 1959); J. of Metals (April 1959).

2. H. A. Robinson, J. R. Doig, M. W. Mote and P. O. Frost. Beta-Omega Age-Hardening Means Stronger Zirconium Alloys, J. of Metals 8, No. 11, 1544 (November 1954).

3. W. Chubb. High-Strength Zirconium Alloy Zr - 4 wt% Zn - 1.6 wt% Mo, Trans. AIME 9, Section 2, 461 (1957); J. of Metals (April 1957).

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CFD/gm

TABLE 1

NOMINAL COMPOSITION		CHEMICAL ANALYSIS				ROOM TEMP MECHANICAL PROPERTIES (SOL. TREATED 750°C)			
Mo wt%	Cu wt%	Mo wt%	Cu wt%	N_2 wt%	W wt%	UTS psi	YS psi	% El	$4\sqrt{\text{area}}$
1.5	1.0	1.48	0.98	0.006	<0.01	107,000	84,000	26	
	1.5	1.53	1.57	0.003	0.06	117,000	101,500	23	
	2.0	1.49	2.02	<0.001	<0.01	104,000	84,000	25	
2.0	1.0	1.96	0.99	0.004	<0.01	105,000	87,500	24	
	1.3	1.94	1.31	0.002	0.05	122,500	102,000	11	
	1.4	1.95	1.37	0.002	0.03	123,000	102,000	22	
	1.5	1.96	1.51	0.009	0.01	125,000	109,000	19	
	1.7	1.95	1.77	0.002	0.03	117,500	100,500	20	
	2.0	1.98	2.05	<0.001	<0.01	110,000	94,000	22	
2.5	1.0	2.47	0.98	0.007	0.01	116,000	104,000	18	
	1.5	2.50	1.51	0.004	0.06	134,000	123,000	17	
	2.0	2.43	1.99	0.001	<0.01	120,000	108,500	21	

TABLE 2

COMPOSITION		HARDNESSES VHN (30 kg Load) SOLUTION TEMPERATURE °C					
Cu wt%	Mo wt%	600	650	700	750	800	850
1.0	1.5	194	192		217	290	446
1.5		200	202	200	233	283	441
2.0		194	185	201	210	268	451
1.0	2.0	196	197	204	217	286	400
1.3		211	203	214	217	304	432
1.4		212	205	218	236	311	470
1.5		235	225	222	260	314	436
1.7		211	208	233	226	313	470
2.0		206	200	225	225	303	429
1.0	2.5	209	209	215	228	312	383
1.5		238	233	252	271	323	366
2.0		228	221	235	252	316	418

Note:- All samples had a preliminary solution heat treatment at 750°C

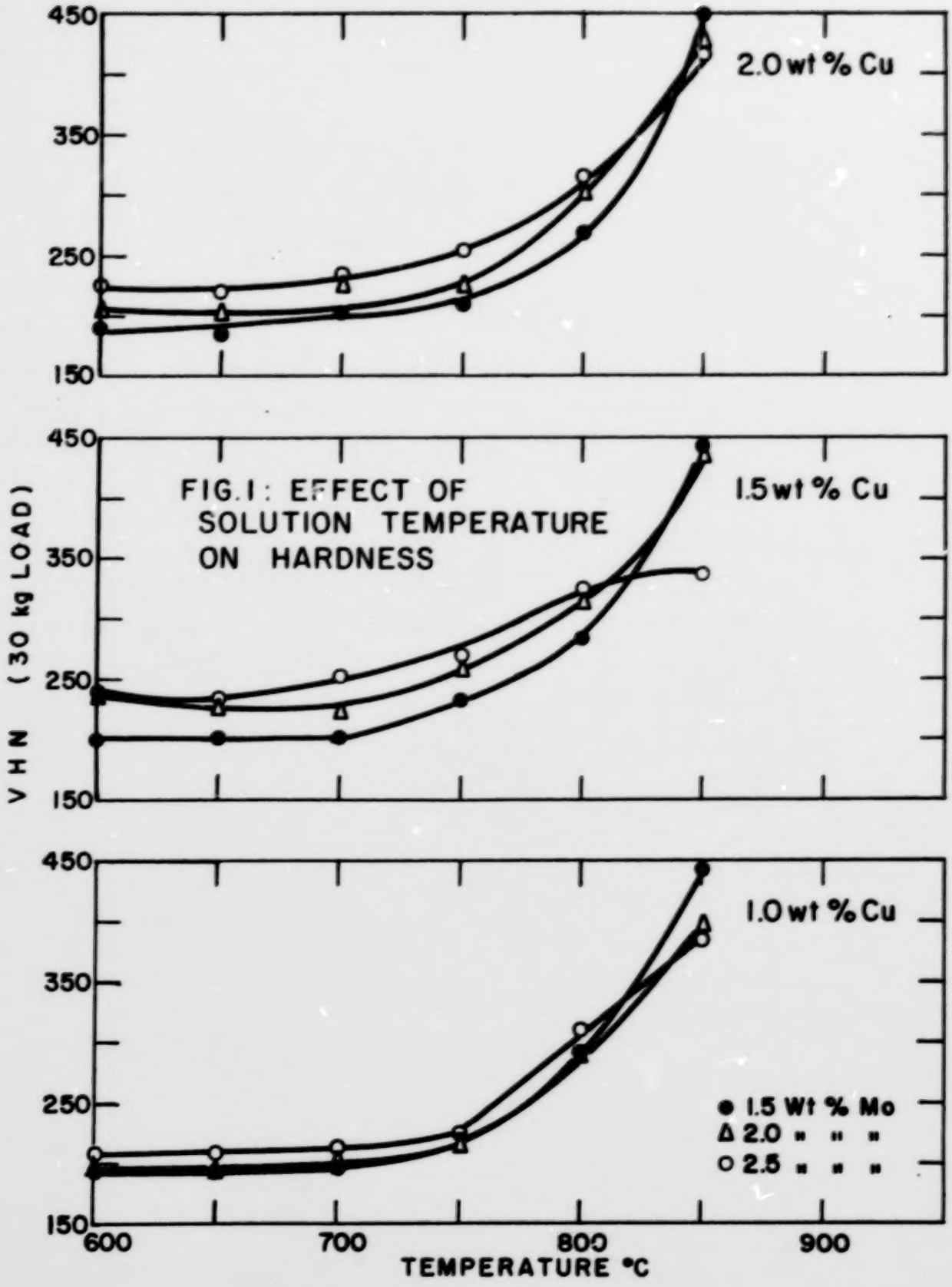


FIG. 1: EFFECT OF SOLUTION TEMPERATURE ON HARDNESS

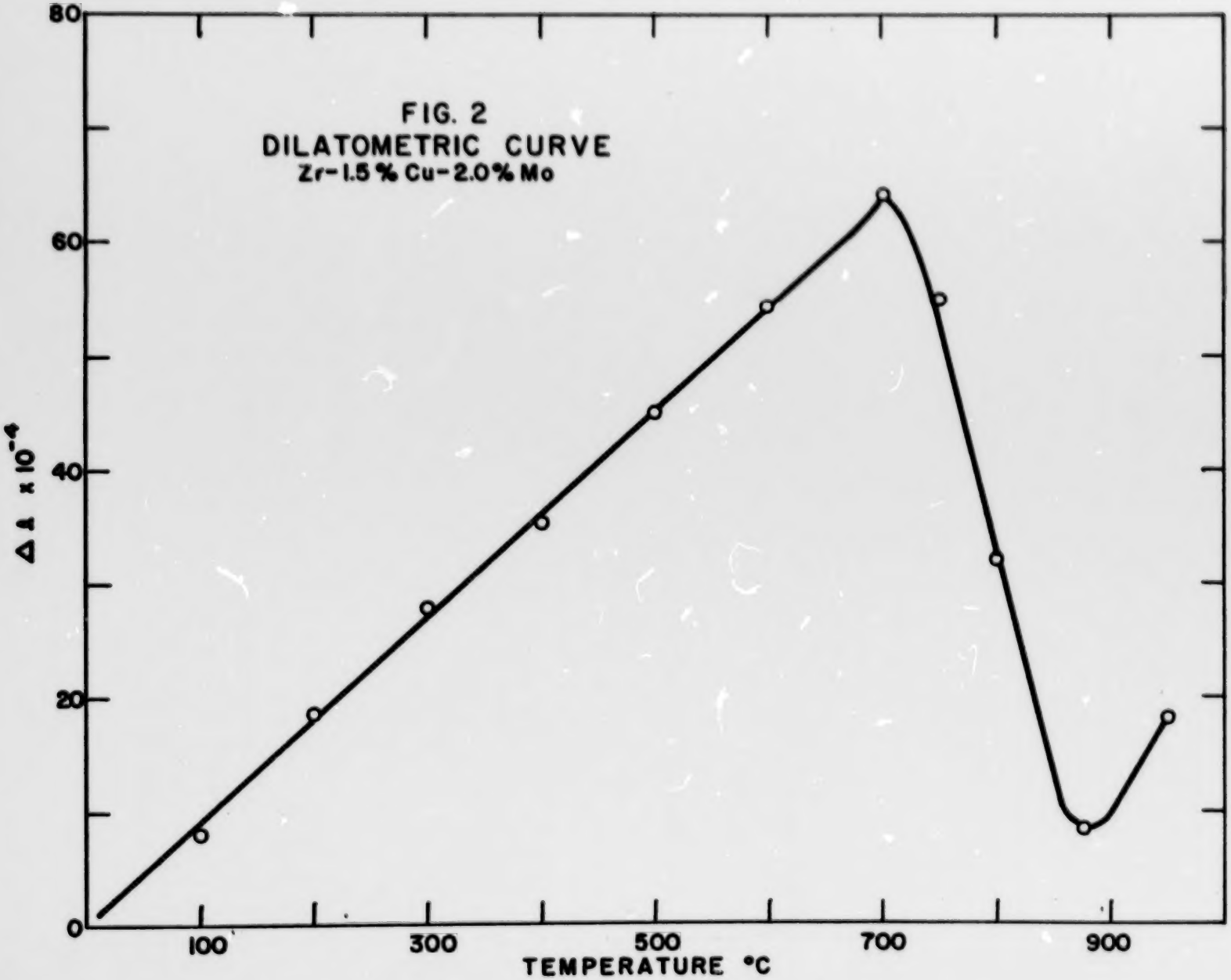
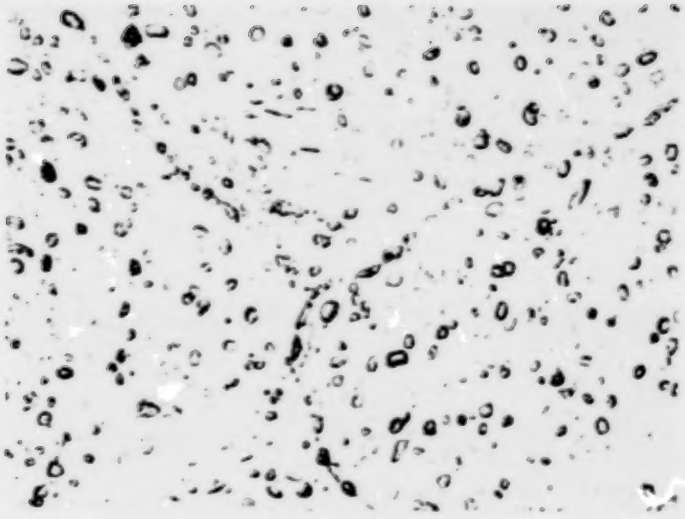
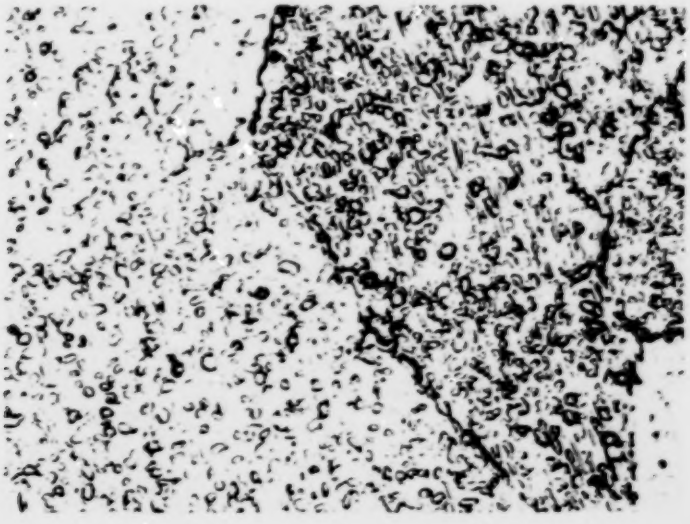


FIG. 2
DILATOMETRIC CURVE
Zr-1.5 % Cu-2.0 % Mo
80
60
40
20
0
Δ ℓ x 10⁻⁴
100
300
500
700
900
TEMPERATURE °C



(Zr - 1.5 wt% Cu - 2.0 wt% Mo; 750X)

Figure 3 - Solution-Treated 850°C (1560°F) Electropolished



(Zr - 1.5 wt% Cu - 2.0 wt% Mo; 750X)

Figure 4 - Solution-Treated 800°C (1470°F) Electropolished

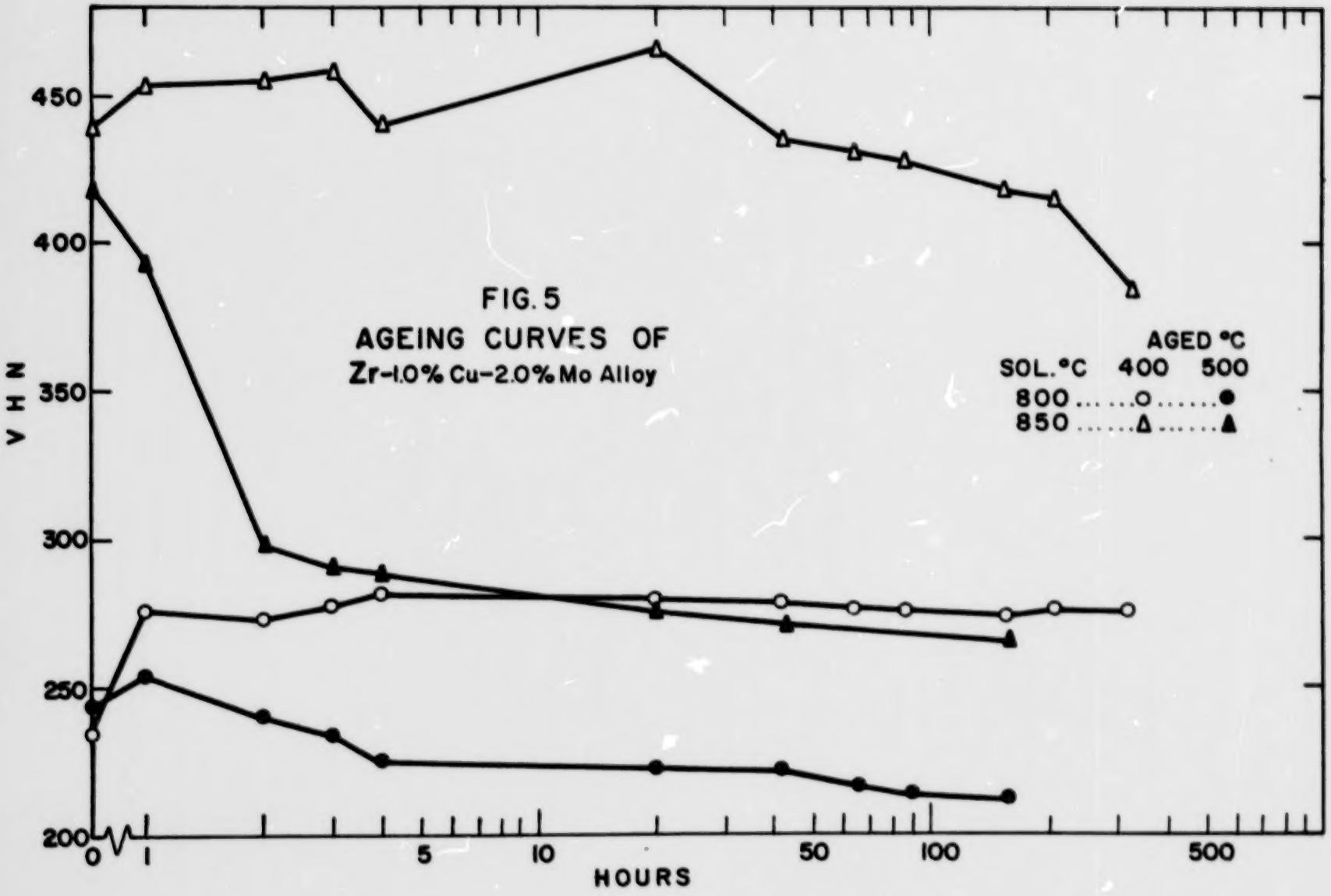


FIG. 5
AGEING CURVES OF
Zr-1.0% Cu-2.0% Mo Alloy
AGED °C
SOL.°C 400 500
800 ..... ○ ..... ●
850 ..... △ ..... ▲
V H N
450
400
350
300
250
200
0
1
5
10
50
100
500
HOURS

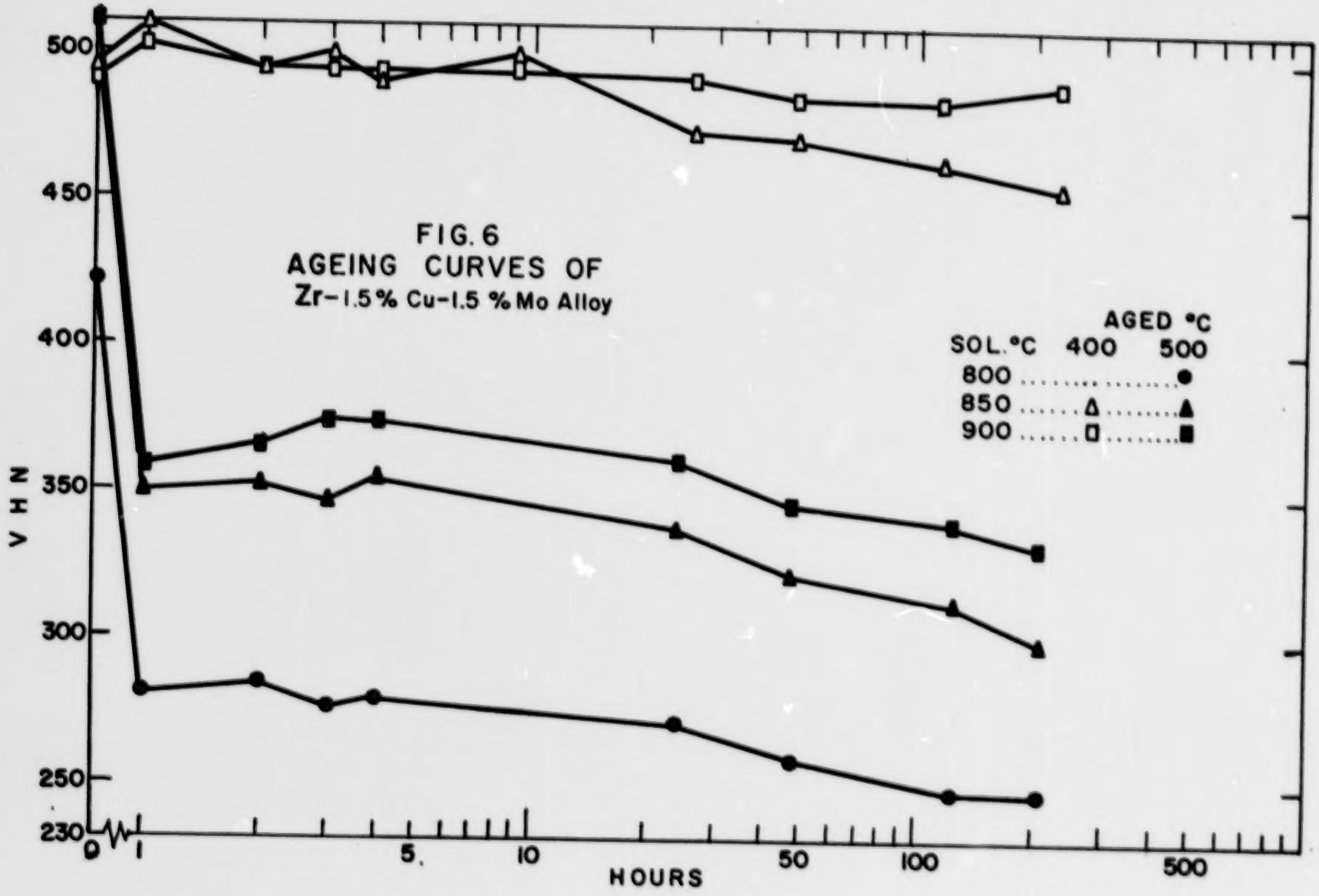


FIG. 6
AGEING CURVES OF
Zr-1.5% Cu-1.5 % Mo Alloy

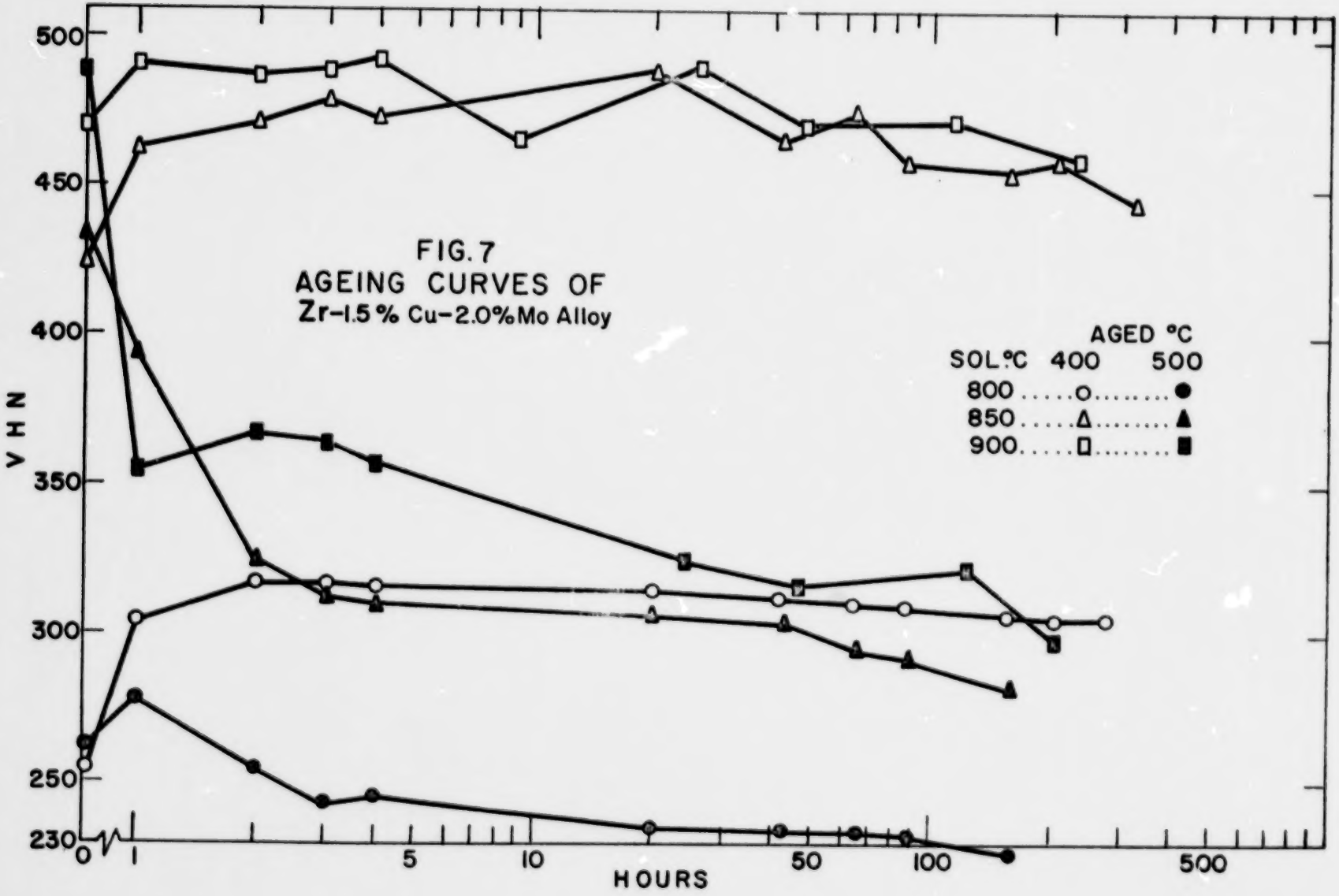


FIG. 7
AGEING CURVES OF
Zr-1.5 % Cu-2.0% Mo Alloy

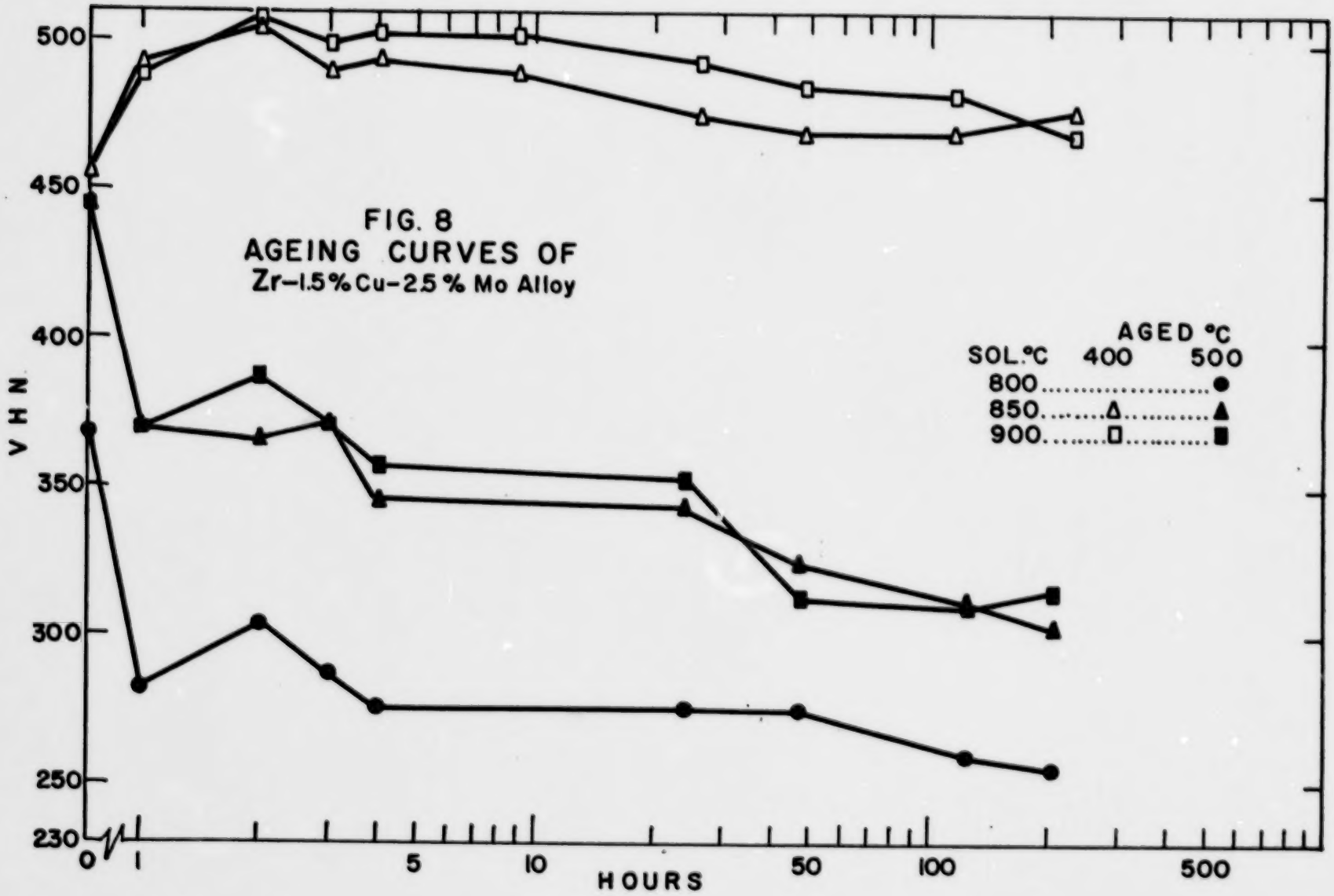


FIG. 8
AGEING CURVES OF
Zr–1.5% Cu–2.5 % Mo Alloy

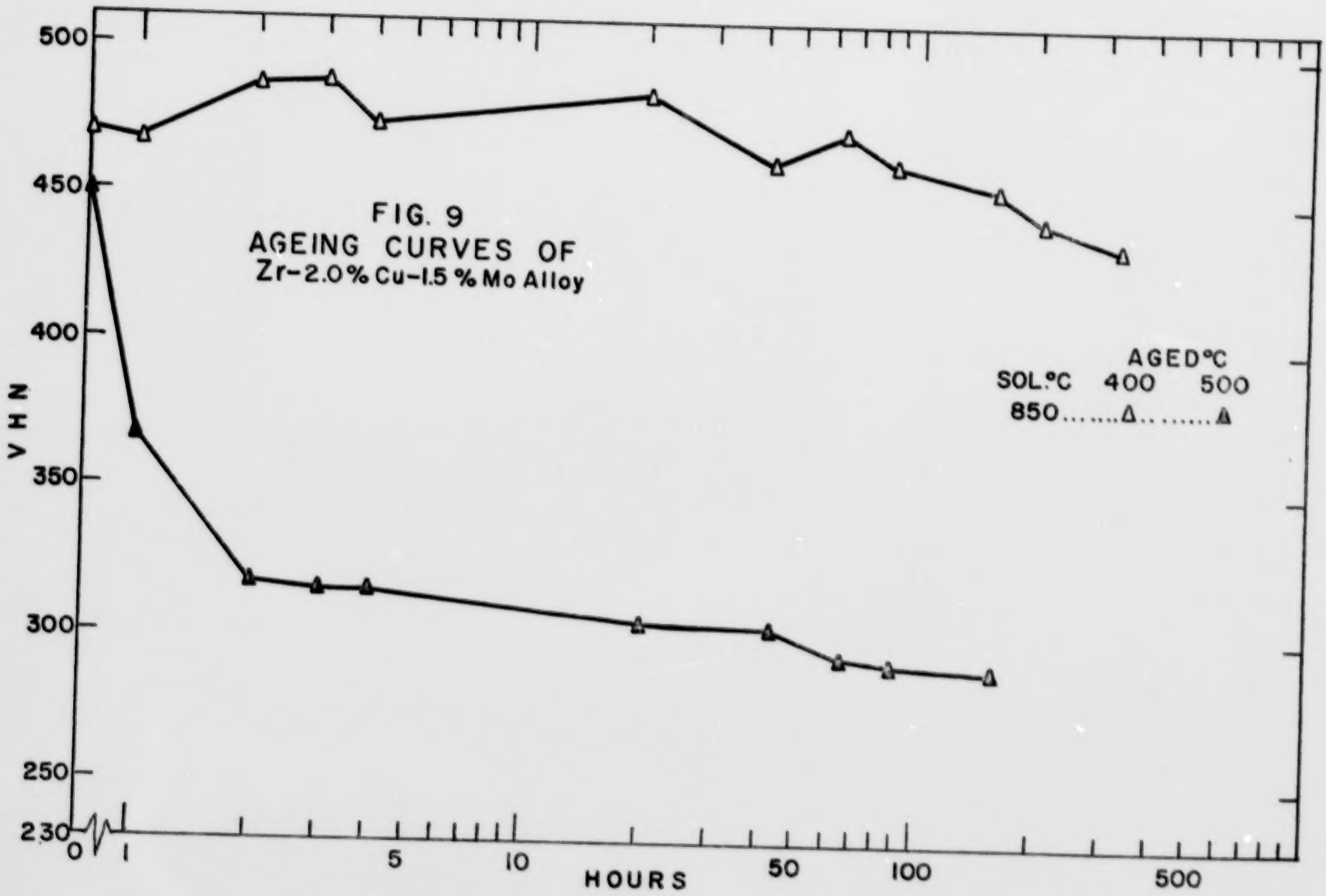


FIG. 9
AGEING CURVES OF
Zr-2.0% Cu-1.5 % Mo Alloy

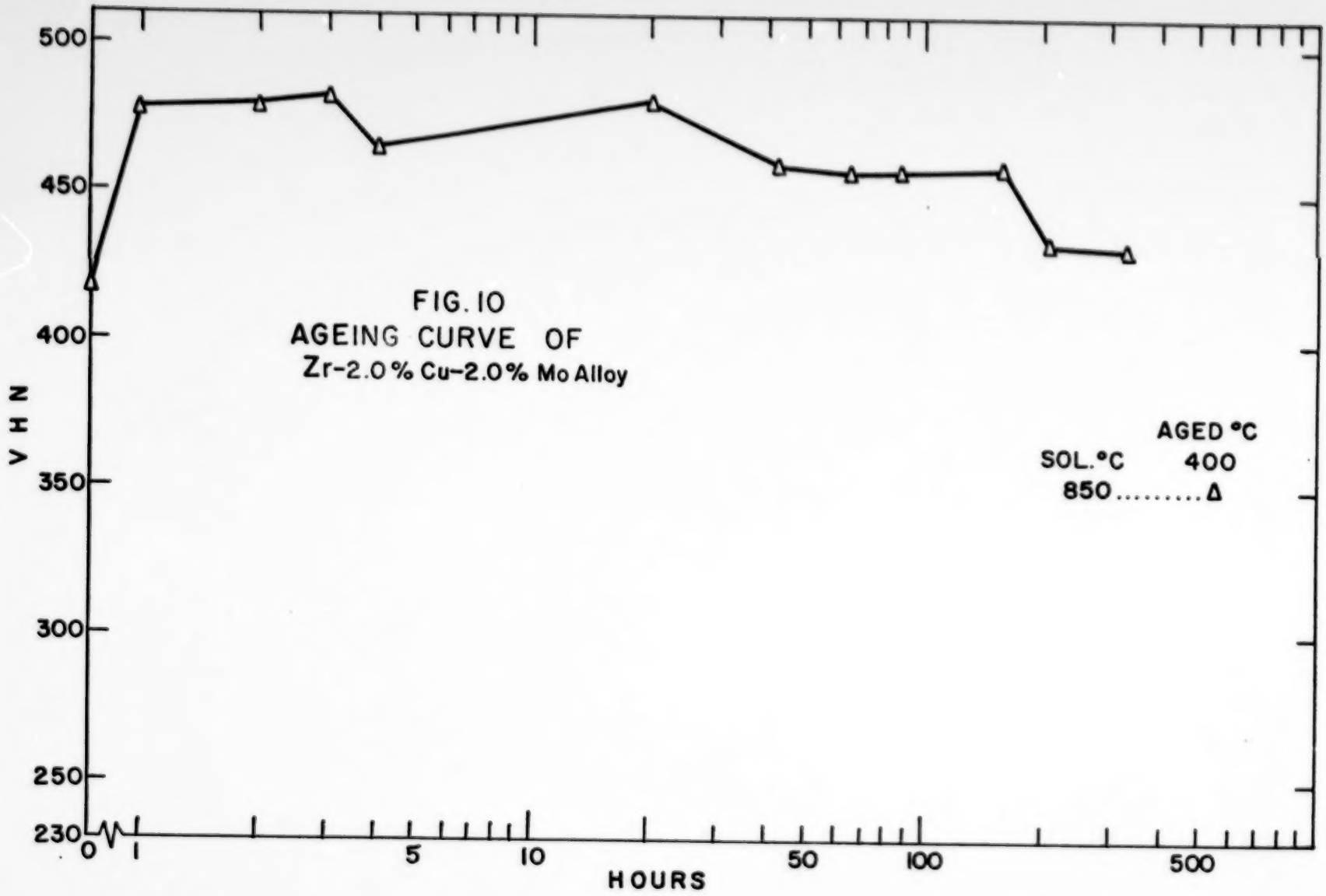
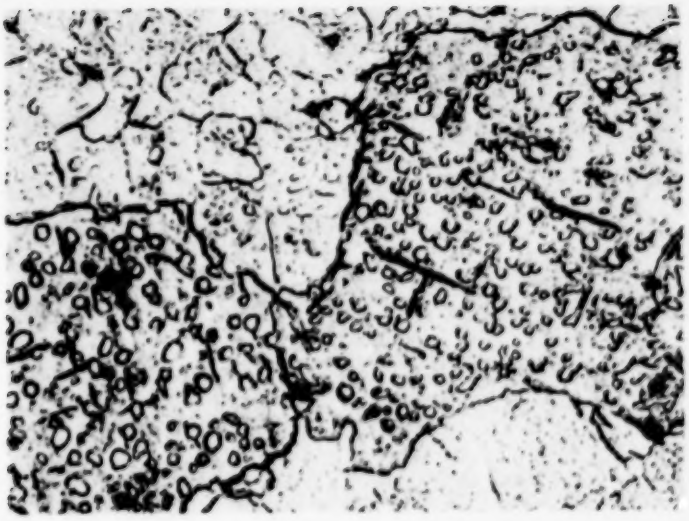


FIG. 10
AGEING CURVE OF
Zr-2.0% Cu-2.0% Mo Alloy



(Zr - 1.5 wt% Cu - 2.0 wt% Mo: 750X)

Figure 11 - Solution-Treated 850°C (1560°F) Aged 400°C (750°F) 200 hours Electropolished

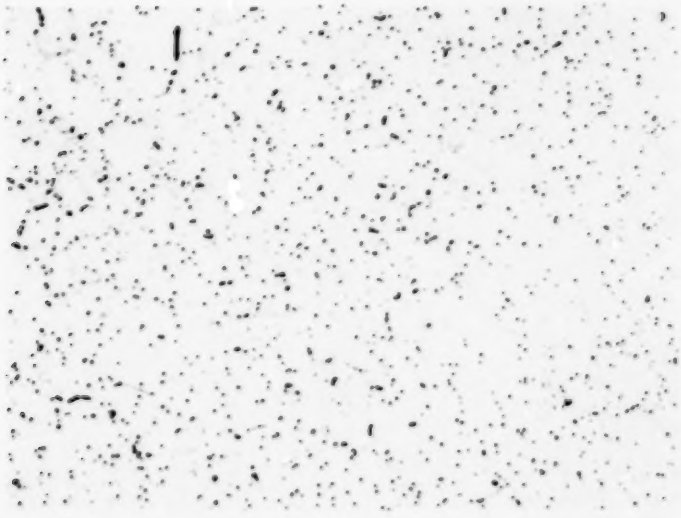


Figure 12 - Solution-Treated 850°C (1560°F) Aged 500°C (930°F) 24 hours Electropolished

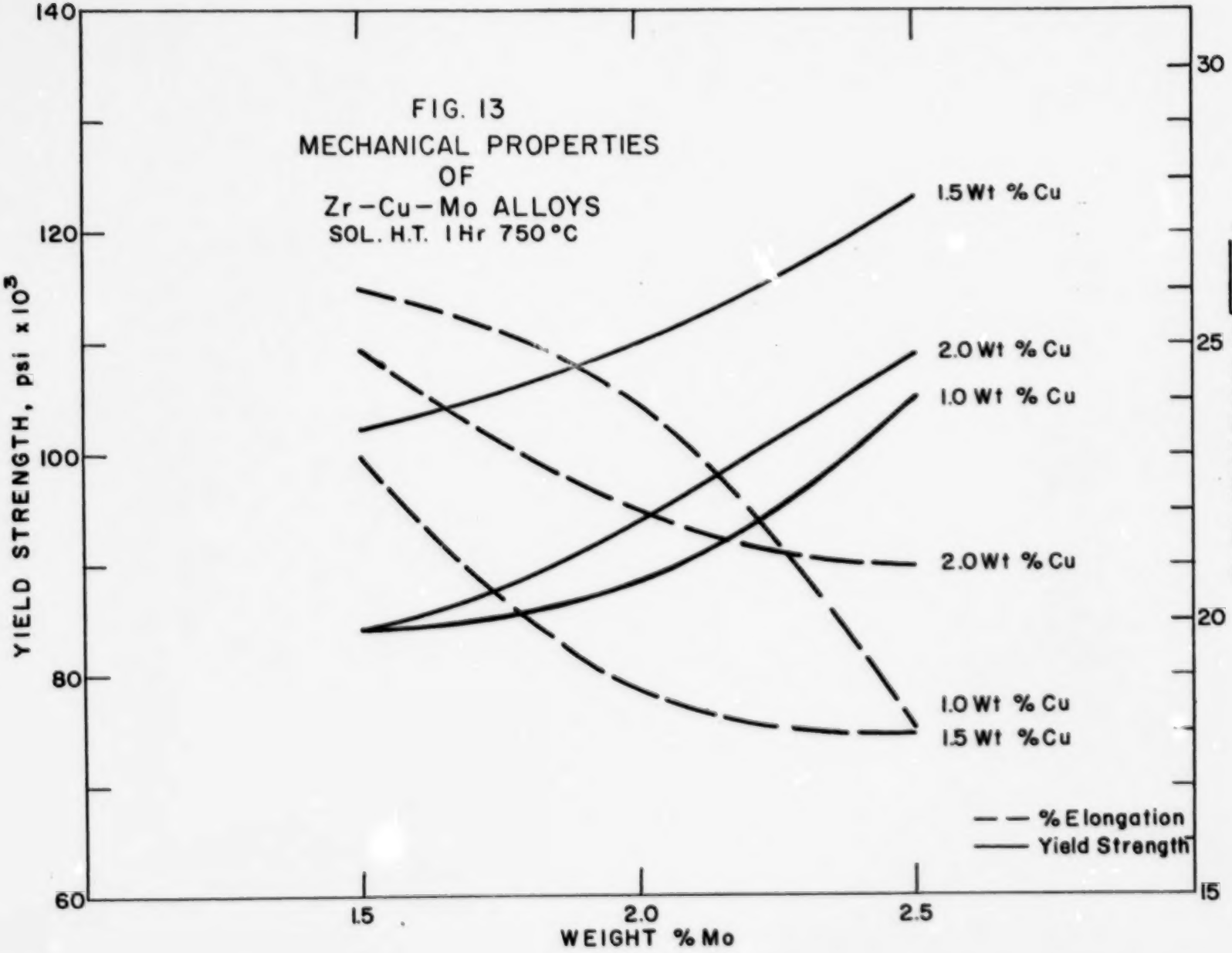


FIG. 13
MECHANICAL PROPERTIES
OF
Zr-Cu-Mo ALLOYS
SOL. H.T. 1 Hr 750°C
YIELD STRENGTH, psi x 10³
% ELONGATION (4√AREA)
WEIGHT % Mo
140
120
100
80
60
30
25
20
15
1.5
2.0
2.5
1.5 Wt % Cu
2.0 Wt % Cu
1.0 Wt % Cu
2.0 Wt % Cu
1.0 Wt % Cu
1.5 Wt % Cu
% Elongation
Yield Strength